

The Role of π -Type Nonbonding Orbitals for Spin–Orbit Induced NMR Chemical Shifts: DFT Study of ^{13}C and ^{19}F Shifts in the Series CF_3IF_n ($n = 0, 2, 4, 6$)

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ABSTRACT: π -type nonbonding orbitals on heavy halogen or related substituents are largely responsible for significantly shielding spin–orbit-induced heavy-atom effects on nuclear magnetic resonance (NMR) chemical shifts of the neighboring atoms. This suggestion has been examined and confirmed by density functional theory (DFT) calculations on ^{13}C shifts of trifluoromethyl compounds CF_3IF_n ($n = 0, 2, 4, 6$), including both one- and two-electron spin–orbit corrections. Indeed, the “removal of iodine π -type lone pairs” upon oxidation leads to a dramatic reduction in the absolute values of the negative ^{13}C spin–orbit shifts along the first three members of the series (-57 , -29 , and 0 ppm for $n = 0, 2$, and 4 , respectively). The inclusion of the spin–orbit effects is mandatory to reach even qualitative agreement between theoretical and experimental trends. Analyses of the shift tensors provide further insight into the spin–orbit effects. In particular, the orientation of the ^{13}C shift tensors for CF_3I and CF_3IF_2 is altered dramatically by spin–orbit coupling. Structural and chemical shift predictions are made for the as yet unknown CF_3IF_6 . Spin–orbit

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effects on ^{19}F shifts for fluorine atoms bound to iodine are much less pronounced than those for carbon shifts. This is related to the low fluorine s-character in the bonds, and thus to a less effective Fermi-contact mechanism. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 1304–1313, 1999

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Introduction

Spin-orbit (SO) effects on nuclear magnetic resonance (NMR) chemical shifts have received increased interest during the past 4 years. The reason is that the accuracy and efficiency of *ab initio*^{1–4} and density functional theory^{5–8} (DFT) approaches to calculate NMR chemical shifts has now arrived at a stage where the application to compounds containing heavier atoms is within reach. Thus, one has to deal with relativistic effects—that is, both with scalar relativistic contributions and with SO coupling. While early work dealing with SO effects on chemical shifts was done at semiempirical levels of theory,^{9,10} various more quantitative methods are now available to compute SO corrections to nuclear shieldings, based on Hartree-Fock^{11,12} or multiconfigurational SCF wave functions,¹² or based on DFT approaches.^{5,13–15}

Comparison with experiment has clearly shown that, in many cases involving heavy elements, the observed shielding trends across a given series of compounds are due predominantly to SO effects caused by the heavy atom substituents (see, e.g., refs. 5–14, 16–19). A typical and well-studied example is the frequently observed “normal halogen dependence” (NHD) of main group chemical shifts; that is, a decrease of the shift in going from Cl to Br to I substituents.²⁰ The NHD of main group chemical shifts has been found to be an SO effect in all cases examined computationally.^{6,9–18} Because we can now compute such SO contributions at a quantitative level, it is obvious to ask whether we may also understand SO influences qualitatively. This would enable us to develop simple models to be used by investigators for the interpretation of spectra. In addition, such qualitative models should also help to evaluate, prior to explicit, potentially expensive quantum-chemical calculations of nuclear shieldings, whether SO effects have to be considered for a specific chemical system of interest.

Toward this end, we recently made use of a simple analogy between the SO contributions to chemical shifts (SO shifts) and the Fermi-contact (FC) mechanism of indirect spin-spin coupling constants.¹⁷ Thus, the spin-orbit-induced electronic spin polarization in the presence of an external magnetic field interacts with the nuclear magnetic moments in a very similar fashion as this is known for indirect spin-spin coupling. This analogy had already been suggested implicitly in the late 1960s by Nakagawa et al.,²¹ and we could confirm the validity of the concept by explicit DFT calculations on a number of iodosubstituted compounds.¹⁷ Thus, for example, the ^1H and ^{13}C SO shifts in iodobenzene were found to exhibit close similarity to the corresponding reduced I–H and I–C spin-spin coupling constants. A Karplus-type relationship was found to hold for three-bond SO shifts, and the s-character of bonding was found to play an important role in the FC-based transfer of the SO-induced spin polarization to the nucleus observed by NMR.¹⁷

One observation we frequently made in MO analyses of the SO contributions for halide substituents¹⁷ is that it is the π -type nonbonding MOs centered on the halogen that appear to be largely responsible for the negative SO contributions to the shifts of the neighboring atoms. Similar conclusions had already been drawn by Pyykkö et al., based on relativistic extended Hückel (REX) calculations.¹⁰ This suggests that the removal or delocalization of such π -type “lone pairs” should lead to a dramatic decrease in the SO shifts. In the present work, we examine this idea by DFT calculations on the ^{13}C and ^{19}F shifts in the CF_3IF_n ($n = 0, 2, 4, 6$) series of molecules, which differ in the formal number of π - and σ -type nonbonding orbitals on iodine. The particular choice of compounds has been motivated by the recent experimental work of Tyrra et al.,²² who examined in detail the ^{13}C and ^{19}F spectra for the first three members of the series (i.e., for $n = 0, 2, 4$). We will examine the influence of SO effects on chemical shift anisotropy, noting in particular how the ori-

entation of the shift tensor may be changed by SO corrections.

Computational Methods

SHIELDING CALCULATIONS

The nuclear shielding calculations were carried out at the sum-over-states density functional perturbation theory (SOS-DFPT) level in its Loc1 approximation,^{5,23} using a modified version of the DeMon-KS program²⁴ augmented by the DeMon-NMR code.⁵ All calculations of SO corrections to the nuclear shieldings, following the third-order perturbation theory approach of refs. 13 and 14, have been obtained with the Perdew–Wang exchange functional²⁵ and the Perdew correlation functional (PP),²⁶ whereas the uncorrected (nonrelativistic) chemical shifts were calculated with the Perdew–Wang exchange–correlation functional (PW91).²⁷ Further computational details can be seen in refs. 13, 14, 16–18. This choice of different exchange–correlation potentials has been our usual procedure in such calculations.^{6,7} It is based on our general experience that the PW91 functional performs somewhat better than other gradient-corrected functionals for nonrelativistic main group chemical shifts, whereas the PP functional is superior to other gradient-corrected functionals for properties involving Fermi-contact interactions.⁵ Test calculations on some of the present systems with the PP functional also for the nonrelativistic shifts indicate that this functional gives systematically larger values by ca. 3–6 ppm for both ¹³C and ¹⁹F shifts and thus would produce a slight deterioration of the results with respect to experiment.

We have mainly used the basis set BII of Kutzelnigg et al.² (also known as IGLO-II; f-functions on iodine were omitted). For ¹³C shifts, which are our primary focus, we also used, for comparison, a very large, fully uncontracted (“UP”) basis derived from Partridge’s basis sets,²⁸ with sizes 16s4p (H), 18s13p4d (C,F), and 27s20p14d (I) (cf. ref. 13 for details). While all six Cartesian components of the d-functions were kept in the nonrelativistic shielding calculations, the s-like contaminant was dropped in the calculations of the SO corrections, for compatibility with the SO integral codes. Auxiliary basis sets for fit of the charge density and exchange–correlation potential were of the sizes (5,1) for H, (5,2) for C and F, and (5,5) for I (*n,m* denotes *n* s-functions and *m* spd-shells with shared exponents²⁴). A FINE angular grid

with 32 (for calculation of chemical shifts) or 64 (for SO corrections) points of radial quadrature^{5,24,29} was employed. The initial finite perturbation for the FC term was taken to be $\lambda = 0.001$.

We compared calculations in which only the one-electron SO operators were included to those that also incorporate the two-electron SO terms via a recently implemented¹⁴ mean-field, one-center approximation. The IGLO choice of gauge origin² was used for the nonrelativistic shielding calculations, whereas a common gauge origin at the iodine nucleus was used to compute the SO corrections. We neglected the spin–dipolar (SD) contribution to the hyperfine terms. For light atom shieldings, the SD term has previously been found to typically contribute less than ca. 2–3% of the FC term.^{11,12} We note in passing that the present calculations of the SO terms employ basis sets of up to 981 basis functions (CF₃IF₆ with the UP basis), without any use of symmetry. The calculation of the two-electron SO integrals for such large basis sets has recently become possible through the mean-field and one-center approximation used, which has been shown to perform very well in this context.¹⁴

Computed absolute ¹³C shieldings have been converted to chemical shifts relative to tetramethylsilane (TMS) using absolute shieldings computed for TMS with the BII basis (187.5 ppm) and with the UP basis (182.4 ppm; this value was obtained via the computed shielding of 189.4 ppm for the secondary standard CH₄), respectively. Because the absolute shielding for the usual ¹⁹F standard CFCl₃ appears to be difficult to compute accurately, the conversion of computed absolute fluorine shieldings to relative shifts used the experimental value of ± 195.6 ppm for the absolute ¹⁹F shielding in CFCl₃.³⁰

SPIN–SPIN COUPLING

The Fermi-contact (FC) contribution to indirect spin–spin coupling constants has been computed using the finite-perturbation theory approach of ref. 31. These calculations neglect any relativistic corrections (which are expected to be notable for couplings to iodine), and we do not consider orbital or spin–dipolar contributions (which may be important for couplings to fluorine). Therefore, the results should be viewed as semiquantitative at best, and are used here only to examine the qualitative analogy between SO shifts and FC spin–spin coupling as detailed in ref. 17. These calculations were restricted to the BII basis set. Integration

grids and other computational parameters were the same as those discussed earlier for the calculations of SO shifts (including the choice of $\lambda = 0.001$), but with the initial finite perturbation on iodine rather than on the NMR nucleus in question (test calculations showed that the results essentially do not depend on this choice).

STRUCTURES

As experimentally determined structures were only available for CF_3I and CF_3IF_4 , all structures used for the shielding calculations have, for consistency, been optimized at the Hartree–Fock level,³² using quasirelativistic effective-core potentials, together with (4s4p1d)/[2s2p1d] and (5s5p1d)/[3s3p1d] valence basis sets for carbon and halogen, respectively.³³ A (4s1p)/[2s1p] basis was employed for hydrogen.³⁴ The optimization results are shown in Figure 1, together with the available experimental data^{35,36} and with the atom labels used later (optimizations for CF_3I and CH_3I were done in C_{3v} symmetry, those for the other CF_3IF_n compounds in C_s). After completion of the present

work, an X-ray diffraction study of solid CF_3IF_2 was reported,³⁷ and thus we may now compare the calculated structures with experiment for all species, except for the as-yet-unknown CF_3IF_6 (Fig. 1a–c, experimental values are in parentheses). Agreement between theory and experiment is generally good, with the largest deviations in bond lengths at around 0.02 Å (except for those bonds belonging to groups that are disordered in the X-ray structure, see Fig. 1). Note that the solid-state structures of both CF_3IF_2 and CF_3IF_4 exhibit noticeable I—F...I intermolecular contacts.^{36,37} This will be of importance in the discussion of chemical shifts for the fluorine atoms involved in these contacts. The structure shown for CF_3IF_2 (Fig. 1b) is a minimum on the potential energy surface. However, at this computational level, the transition state for CF_3 group rotation, which also has C_s symmetry, is only 1.4 kJ/mol higher in energy. This indicates almost free rotation, consistent with the disorder found in the solid-state structure.³⁷ We discuss only averaged chemical shift values for those fluorine atoms that are made equivalent by the rotation. For CF_3IF_4 , the computed rotational

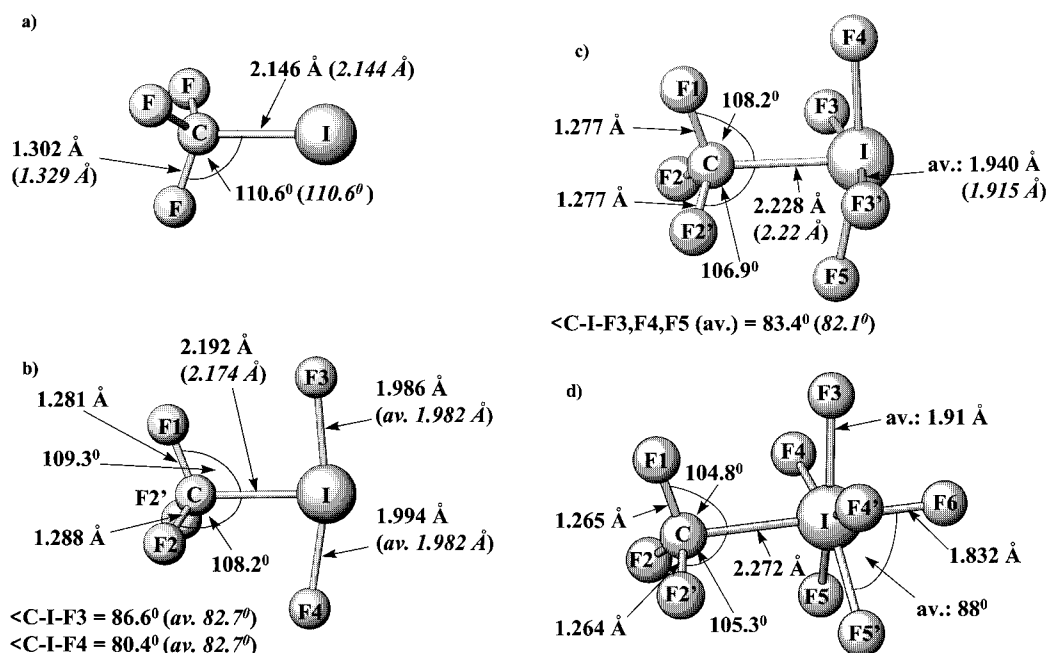


FIGURE 1. Optimized structures and atom labels used in the discussion. Experimental data are given in parentheses (in italics). (a) CF_3I . Experimental data obtained from microwave spectroscopy in the gas phase.³⁵ (b) CF_3IF_2 . Experimental data from solid-state X-ray diffraction.³⁷ Experimental C—F bond lengths (of disordered CF_3 groups) range from 1.235 Å to 1.352 Å, F—C—I angles from 106.2° to 112.9°. (c) CF_3IF_4 . Experimental data from solid-state X-ray diffraction.³⁶ Experimental C—F bond lengths (with significant thermal motion of the fluorine atoms) range from 1.25 Å to 1.28 Å, F—C—I angles from 110° to 112°. (d) CF_3IF_6 .

barrier is even lower, probably below the numerical accuracy permitted by the numerical integrations used in the DFT calculations.

Results and Discussion

^{13}C SHIFTS

Table I summarizes the ^{13}C shifts obtained with both the UP and BII basis sets, with and without SO corrections. The experimental data available for the first three members of the CF_3IF_n series ($n = 0, 2, 4$) are included as well. Figure 2 provides a graphical comparison of computed and experimental data, and it also shows schematically the removal of iodine lone pairs with increasing n .

Obviously, the experimentally observed increase of the ^{13}C shifts with increasing oxidation of the IF_n substituent (i.e., with increasing n) is due to the diminishing SO effects from $n = 0$ through $n = 4$. The nonrelativistically calculated shifts decrease somewhat from $n = 0$ through $n = 4$ and increase very slightly from $n = 4$ to $n = 6$ (a similar trend is found for the fluorine shifts of the CF_3 groups, and the reasons for this will be discussed in the next subsection). The remarkably large SO corrections invert this trend up to $n = 4$, and thus the experimental behavior is recovered. We see slightly better agreement with experiment when using the larger UP basis set. The nonrelativistic value for CF_3IF_4 is improved (increased) with the larger basis (the SO contributions being small in this case). In addition, the larger SO contributions increase the slope of the curve somewhat and thus also improve the agreement with experiment (the largest discrepancies still occur for CF_3I , which also shows the largest SO shifts). However, the overall trends are already reproduced satisfactorily with the smaller BII basis.

TABLE I.
Computed and Experimental Isotropic ^{13}C Shifts.^a

	$\delta_{\text{nonrel.}}$	1-el.-SO	1 + 2-el.-SO	$\delta_{+1\text{-el.-SO}}$	$\delta_{+1+2\text{-el.-SO}}$	Exp. ^b
CH_3I	+1.3 (−1.1)	−35.0 (−29.0)	−32.6 (−27.0)	−33.7 (−30.1)	−31.3 (−28.3)	−21.8
CF_3I	+146.9 (+141.3)	−62.1 (−50.0)	−57.4 (−46.6)	+84.8 (+91.3)	+89.5 (+94.7)	+79.5
CF_3IF_2	+140.0 (134.6)	−30.1 (−25.9)	−27.4 (−23.7)	+109.9 (+108.7)	+112.6 (+110.9)	+106.7
CF_3IF_4	+132.9 (+128.1)	−0.2 (−2.0)	−0.2 (−1.5)	+132.7 (+126.1)	+132.7 (+126.6)	+131.2
CF_3IF_6	+134.8 (+129.6)	−1.2 (−1.1)	−0.7 (−0.7)	+133.6 (+128.5)	+134.1 (+128.9)	—

^aIn ppm vs. TMS. UP basis results with BII basis results in parentheses.

^bIn acetonitrile solution.²²

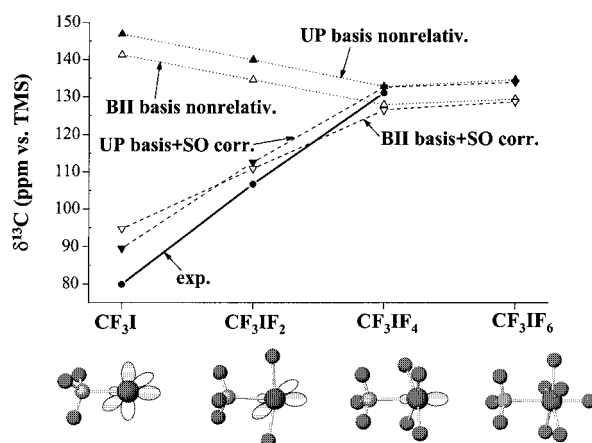


FIGURE 2. Comparison of computed and experimental ^{13}C shifts. SO-corrected data include both one- and two-electron contributions (cf. Table I). BII and UP basis results are compared. Experimental data in acetonitrile solution.²² At the bottom of the figure, the presence of iodine lone pairs is shown schematically.

As expected, the two-electron SO contributions reduce the negative ^{13}C SO shifts by ca. 7–9% (UP basis results) for those cases with significant SO effects (CH_3I , CF_3I , CF_3IF_2). Similar results have been obtained previously for CH_3I and HI at both DFT¹⁴ and MC-SCF levels¹² of theory. Larger relative two-electron contributions (but, of course, smaller absolute ones) are found with lighter halogen substituents.^{12, 14}

At the UP basis level, the SO contributions of −27.4 ppm in CF_3IF_2 (including both one- and two-electron SO terms) are only half those of CF_3I (−57.4 ppm), and those in CF_3IF_4 and CF_3IF_6 are negligible. These results suggest, to a first approximation, that the SO contribution of one π -type lone pair on iodine to the ^{13}C shifts in these systems is roughly ca. −27 ppm, whereas the contributions from the σ -type lone pair are small (cf. schematic orbital description in Fig. 2).

This preliminary picture is borne out by our canonical MO analyses of the SO shifts (at the UP basis level), with only minor modifications: In CF_3I , the degenerate HOMO (corresponding to the two π -type nonbonding orbitals on iodine) accounts for the entire SO shift of ca. -57 ppm, with several small contributions from other MOs canceling each other. In CF_3IF_2 , the dominant contribution (ca. -23 ppm of ca. -27 ppm) comes again from the HOMO, which corresponds indeed to the single π -type nonbonding electron pair on iodine. Among the remaining, smaller contributions, one MO with predominantly π -type lone pair character of the fluorine atoms within the CF_3 group accounts for ca. -9 ppm (some still smaller, positive contributions arise from several other orbitals). For CF_3IF_4 , the HOMO corresponds to the remaining G-type lone pair on iodine (with some I—C bonding character). This MO accounts for an SO shift of ca. ± 9 ppm. This positive shift is almost exactly compensated by negative contributions from two lower lying MOs with significant fluorine π -type lone pair character of the CF_3 group [and with some additional antisymmetric $\sigma(\text{I—F})$ bonding character within the IF_4 unit]. No individual MO contributions of more than ca. 3–4 ppm to the SO shifts are apparent for CF_3IF_6 , for which the overall SO shifts are almost negligible.

We note, in passing, that the overall SO contributions in CF_3I (-57.4 ppm) are almost twice as large as those in CH_3I (-32.6 ppm), although the fluorine lone pair contributions can account for, at most, a few ppm. As discussed in ref. 17, the electronegative fluorine substituents in CF_3I withdraw charge from the central carbon atom and thus increase the carbon 2s character of the I—C bond. This enhances the FC mechanism for the transfer of spin polarization and thus the overall SO contributions significantly.

We may also ask about the influence of the SO contributions on the anisotropy of the shifts. Early relativistic extended Hückel (REX) calculations¹⁰ of the ^1H shifts in hydrogen iodide have shown that the SO contributions arise entirely via the tensor components perpendicular to the threefold symmetry axis (δ_\perp), with no contribution to the parallel component (δ_\parallel), due to symmetry reasons. The shift anisotropy is therefore altered dramatically. Similar conclusions were drawn for the ^{13}C shifts of the methylhalides.¹⁰

In the case of CF_3I , we also have axial symmetry of the shift tensor and thus may still obtain a reasonably straightforward interpretation. Thus, at the nonrelativistic level (UP basis), the parallel

shift tensor component is $\delta_\parallel = 129.0$ ppm, and the perpendicular components $\delta_\perp = 156.0$ ppm (within a localized MO framework, the paramagnetic shielding contributions to δ_\parallel and δ_\perp arise largely from C—F and I—C bonding MOs). This picture is altered significantly by the SO shifts (one- and two-electron SO contributions included), resulting in $\delta_\parallel = 126.3$ ppm and in $\delta_\perp = 71.3$ ppm; that is, the SO contributions reduce the shifts predominantly (but not exclusively as for the ^1H shifts in the linear molecule HI) via a reduction of δ_\perp by 84.7 ppm. Qualitatively similar results have also been found at the REX level for CH_3I ,¹⁰ and this behavior is exactly what is expected from an SO-induced coupling between the iodine π -type nonbonding MOs and a $\sigma(\text{I—C})$ antibonding MO, as found in our MO analyses of the SO shifts (the small SO contributions of -2.7 ppm to δ_\parallel arise from fluorine lone-pair-type MOs). The early REX analyses for HI (or for CH_3I) further suggest a significantly deshielding SO contribution from the I—H (or I—C) σ -bonding MO, which partially compensates the shielding contributions from the π -type lone pairs.¹⁰ However, in our MO analyses at the DFT level, such σ -type nonbonding MO contributions are at least one order of magnitude smaller than those arising from the iodine π -type lone pairs.

The description is already more complicated for CF_3IF_2 , where we have only C_s symmetry (cf. Fig. 1b). At the nonrelativistic level (UP basis), the computed anisotropy of the shift is small, with $\delta_{11} = 146.7$ ppm, $\delta_{22} = 136.8$ ppm, and $\delta_{33} = 136.4$ ppm. Figure 3a shows the orientation of the corresponding absolute shielding tensor (σ) relative to the molecular framework, and the Cartesian axes used (note the different sign conventions for σ and δ). σ_{11} points along the x -direction; that is, it is perpendicular to both the π -type lone pair on iodine and to the I—C bond vector. The other two components arise from linear combinations of components lying in the yz plane. In contrast, the SO contributions are essentially diagonal in the Cartesian axes system shown, with the largest contribution $\sigma_{xx}(\text{SO}) = +79.5$ ppm, as well as $\sigma_{yy}(\text{SO}) = -4.0$ ppm and $\sigma_{zz}(\text{SO}) = +6.6$ ppm. As a result, the SO-corrected shift tensor σ has $\delta_{11} = 142.0$ ppm, $\delta_{22} = 130.1$ ppm, and $\delta_{33} = 65.9$ ppm. The corresponding absolute shielding tensor σ is shown in Figure 3b. Due to the large SO contribution to σ_{xx} , the latter now corresponds essentially to σ_{33} . σ_{11} is now close to the y -direction, and σ_{22} points almost exactly along the z -axis. The large, negative SO contribution to σ_{xx} is

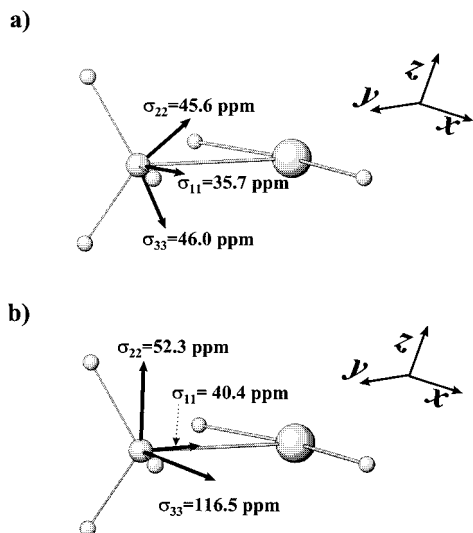


FIGURE 3. Schematic description of the orientation of the ^{13}C absolute shielding tensor in CF_3IF_2 relative to the molecular framework, with a Cartesian axis system used. UP basis results: (a) nonrelativistic calculation; (b) one- and two-electron SO corrections included.

completely consistent with a coupling between the remaining single iodine π -type lone pair (oriented along z) and a $\sigma(\text{I}-\text{C})$ antibonding MO (oriented along y). This is confirmed by our MO analyses. Shift anisotropies are small for CF_3IF_4 and CF_3IF_6 , and they are not influenced very much by SO effects. Thus, we omit a presentation of detailed analyses of the shift tensors for the latter two systems.

In ref. 17, we stressed the usefulness of an analogy between the FC mechanism for the transfer of SO-induced spin polarization and that of indirect spin-spin coupling constants. It was shown that structural and electronic changes in the environment of the NMR nucleus probed affect SO shifts and reduced spin-spin coupling constants in a similar way. Figure 4 compares the ^{13}C SO shifts and the FC part of the reduced I—C coupling constants $^1K_{\text{FC}}(\text{I},\text{C})$ for CH_3I , and for the CF_3IF_n series of molecules. In going from CH_3I to CF_3I , the two quantities obviously correlate quite well. However, starting with CF_3IF_2 , we change the direct electronic environment of the heavy atom substituent (by “removing” iodine nonbonding orbitals). Consequently, the analogy ceases to hold. In particular, while the SO shifts are already negligible for both CF_3IF_4 and CF_3IF_6 , due to the lack of π -type lone pairs on iodine, the reduced coupling constants still change significantly, from $+160.7 \times 10^{19} \text{ NA}^{-2} \text{ m}^{-3}$ for CF_3IF_4 to $+743.6 \times 10^{19} \text{ NA}^{-2}$

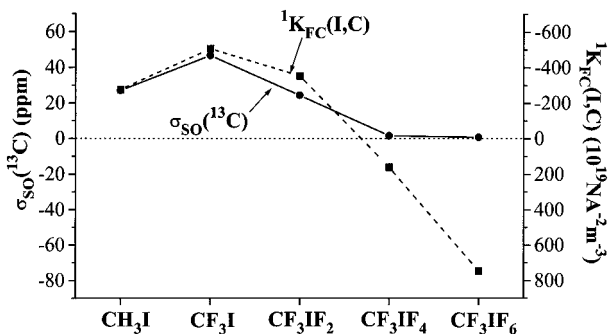


FIGURE 4. Comparison of SO contributions to ^{13}C shielding constants, σ_{SO} , and Fermi-contact contributions to the reduced coupling constants, $^1K_{\text{FC}}(\text{I}-\text{C})$. BII basis results.

m^{-3} for CF_3IF_6 . The removal of the remaining σ -type nonbonding electron pair in going from CF_3IF_4 to CF_3IF_6 does not affect the SO shifts much. However, the iodine s -character of the I—C bond is enhanced significantly. MO analyses clearly indicate that the iodine σ -type nonbonding MO provides a significant negative contribution to the reduced coupling I—C constants in CF_3IF_4 but is not much involved in the ^{13}C SO shifts. Obviously, such effects are not covered by the analogy in ref. 17.

^{19}F SHIFTS

Table II summarizes computed and experimental ^{19}F shifts obtained with the BII basis. Computed values have been averaged for nuclei that are made equivalent by rapid rotation of the CF_3 groups. We start with the CF_3 groups, where SO corrections are essentially negligible in all cases. The calculations overestimate the measured shifts by ca. 10–25 ppm, but reproduce the observed trends reasonably well (see Fig. 5; the computed slope is too negative). The shifts decrease from CF_3I to CF_3IF_4 , but increase very slightly from CF_3IF_4 to CF_3IF_6 . A similar behavior is exhibited by the nonrelativistically calculated ^{13}C shifts (see previous section and Fig. 2).

Part of the trends is due structural changes along the series. Upon oxidation of the iodine center, the coordination number around iodine increases in steps of two and, correspondingly, the I—C bond expands (Fig. 1). As a consequence, the C—F bonds contract (also Fig. 1). We can examine the effect of these structural changes by keeping the structure of the CF_3I fragment frozen to that of CF_3I itself. We obtain $^{19}\text{F}(\text{CF}_3)$ shifts of $+17.9$,

TABLE II.
Computed and Experimental Isotropic ^{19}F Shifts.^a

Molecule	Group	$\delta_{\text{nonrel.}}$	1-el.-SO	1 + 2-el.-SO	$\delta_{+1\text{-el.-SO}}$	$\delta_{+1+2\text{-el.-SO}}$	Exp. ^b
CF_3I		+17.9	−0.1	+0.3	+17.8	+18.2	−7.5
CF_3IF_2	CF_3	−17.6	−0.6	−0.3	−18.2	−17.9	−34.8
	IF_2	−89.0	+4.3	+4.2	−84.7	−84.8	−176.4
CF_3IF_4	CF_3	−49.7	−0.6	−0.3	−50.3	−49.4	−57.9
	IF_4	+33.2	−0.9	−0.8	+32.3	+25.8	−36.5
CF_3IF_6	CF_3	−30.2	+0.3	+0.6	−29.9	−29.6	—
	IF_6 (ax.)	+206.8	−7.7	−6.9	+199.1	+199.9	—
	IF_6 (eq.)	+92.3	−8.4	−7.6	+83.9	+84.7	—

^aIn ppm vs. CFCl_3 . BII basis results. The shifts for the CF_3 groups, the IF_2 group in CF_3IF_2 , the IF_4 group in CF_3IF_4 , and the equatorial atoms of the IF_6 group in CF_3IF_6 have been averaged.

^bIn acetonitrile solution.²²

−9.8, −36.8, and −14.0 ppm for $n = 0, 2, 4, 6$, respectively, compared with +17.9, −17.6, −49.7, and −30.2 ppm for the fully optimized structures. Thus, the changes become less pronounced. Similarly, the ^{13}C shifts (nonrelativistic basis BII results) vary only 141.3, 137.6, 131.3, and 133.0 ppm for the partly frozen structures, compared with 141.3, 134.6, 128.1, and 129.6 ppm for the fully optimized structures (also see Tables I and II).

However, further effects beyond these structural influences are obviously taking place, which are more difficult to analyze. It appears that it is mainly the destabilization of the $\text{C}=\text{F}$ σ^* -type MOs with increasing n , which reduces paramagnetic contributions to both $^{19}\text{F}(\text{CF}_3)$ and ^{13}C shifts. We analyzed the localized (occupied) MO (LMO) contributions to the nonrelativistic ^{19}F shieldings (calculated at the DFT-IGLO level). Of those LMOs coupled by the magnetic-field perturbation to the aforementioned $\text{C}=\text{F}$ σ^* -type virtual MOs, it is

mainly the fluorine lone pair LMO contributions that are rendered smaller. An inversion of the trend is found from CF_3IF_4 to CF_3IF_6 , where all contributions increase slightly. In the case of the ^{13}C shifts, the major contributions that decrease with increasing n , are due to the $\text{I}=\text{C}$ bonding and iodine lone pair LMOs.

We now turn to the fluorine atoms bound directly to iodine. The computed SO corrections range from +4.8 ppm in CF_3IF_2 to −7.6 ppm in CF_3IF_6 (two-electron contributions included, see Table II). These relatively small one-bond SO shifts contrast markedly with the much larger ones discussed earlier for the ^{13}C shifts. The reason is that, in contrast to the significant carbon s-character of the $\text{I}=\text{C}$ bonds, the $\text{I}=\text{F}$ bonds have rather little fluorine s-character, due to the concentration of s-character in the fluorine σ -type lone pair. As discussed previously (see also Introduction), a large s-character is necessary to allow an efficient Fermi-contact mechanism for the transfer of the spin-orbit-induced spin polarization to the NMR nucleus.¹⁷ As fluorine uses relatively little valence s-character in most bonding situations, we expect that fluorine SO shifts will generally not be very pronounced. In contrast, hydrogen shifts have been found to be particularly sensitive to SO effects, as the hydrogen s-character predominates the bonding.^{17,19}

Agreement with experimental shifts is poor for the fluorine atoms bound to iodine. The computed shifts (with SO corrections) are too large by ca. 91 ppm for CF_3IF_2 , and by ca. 60 ppm for CF_3IF_4 . These discrepancies are outside the expected systematic errors of the computational methods used. We suspect that they are due to specific inter-

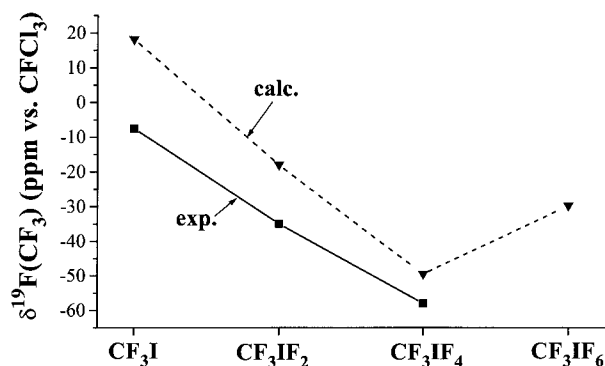


FIGURE 5. Comparison of computed and experimental $^{19}\text{F}(\text{CF}_3)$ shifts. The calculations include both one- and two-electron SO corrections, using the BII basis. Experimental data in acetonitrile solution.²²

molecular interactions of the IF_n groups, either with other solute molecules or, most likely, with the acetonitrile solvent. In the solid-state structures of both compounds, significant intermolecular $\text{I}\cdots\text{F}\cdots\text{I}$ interactions are apparent.^{36,37} The larger deviation from experiment for CF_3IF_2 would then also be consistent with the expected larger $\text{I}\cdots\text{F}$ bond ionicity (as confirmed by our population analyses), and thus with particularly pronounced solvent coordination for this molecule. Both the coordination of solvent nitrogen donor atoms to iodine or of solute IF_n fluorine donors to the solvent might be envisioned. Computational studies on model complexes may shed light on this question but are beyond the scope of the present work. It is clear that the ^{19}F and ^{13}C shifts of the CF_3 groups will be much less affected by these intermolecular interactions, as borne out by the results.

Conclusions

This case study has provided further understanding of the mechanisms of spin-orbit-induced heavy atom effects on NMR chemical shifts. The early suggestion of the importance of π -type lone pairs on heavy halogen or related substituents by Pyykkö et al.¹⁰ has been confirmed. By studying a series of closely related molecules that differ mainly in the number of π -type and σ -type lone pairs on iodine, the dependence of the shift/shielding tensors on SO-induced couplings between occupied and virtual MOs has been clarified. We note, in particular, that the SO corrections may be strongly anisotropic and can thus alter significantly the orientation of the shift tensor, as shown here for CF_3I and CF_3IF_2 .

We have previously emphasized the importance of an efficient Fermi-contact-type mechanism for the transfer of SO-induced spin polarization to the nuclei within the system.¹⁷ The present study has highlighted that the efficient coupling of suitable high-lying occupied and low-lying unoccupied MOs by the other two perturbations involved (SO coupling and external magnetic field) is also necessary for significant SO chemical shifts. We also showed that the analogy between SO shifts and indirect spin-spin coupling constants delineated in ref. 17 will be less useful when changing significantly the electronic structure of the direct neighborhood of the heavy atom "spin-orbit centers."

Although the inclusion of SO effects is obviously mandatory if one intends to reproduce the

experimentally observed trends of ^{13}C shifts from CF_3I through CF_3IF_4 , the calculations indicate only minor SO effects for the carbon shifts of the as-yet-unknown iodine(VII) compound CF_3IF_6 (and for CF_3IF_4), due to the lack of iodine π -type lone pairs. Both the ^{13}C and $^{19}\text{F}(\text{CF}_3)$ shifts for this system are predicted to be slightly larger than those for the corresponding iodine(V) species, CF_3IF_4 . The ^{13}C shifts for CF_3IF_6 should thus invert the SO-dominated decrease in the carbon shifts found for the first three members of the CF_3IF_n ($n = 0, 2, 4, 6$) series.

Finally, we note that SO effects on ^{19}F shifts of fluorine atoms attached to the iodine substituent have been found to be much smaller than those on the ^{13}C shifts. This is due to the small contributions from s-orbitals on fluorine to the $\text{I}\cdots\text{F}$ bonds. We generally expect that SO shifts are moderate or small for fluorine, whereas they tend to be particularly large for hydrogen.¹⁷

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